

Studies on new ion-exchange resin for effluent treatment of metal industries

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ABSTRACT

The polyamine (PA) was prepared by condensation of 1, 4-bis(chloromethyl) benzene and 1, 4-benzene diamine. The PA was then treated with cyanuric chloride at 0°C followed by reaction with sulfanilic acid in THF in concentrated NaOH (pH 9-10) at room temperature for 8 hrs. The resultant polymer designated as polyamine-s-triazine-sulfanilic acid (PATS) was characterized by elemental analysis, IR spectral studies, and thermogravimetry. The PATS sample was monitored for its ion-exchanging properties. Batch equilibration method has been adopted, for such properties. Based on this the PATS resin was employed for removing the metal ions from effluent coming out of electroplating industry.

Key words: Polyamines, s-triazine, Sulfanilic acid, ion-exchange properties, Batch equilibrium method, thermogravimetry.

INTRODUCTION

The effluents from mines and metal industries set up the serious problems in removal of heavy toxic metal ions. The contents of these metals in effluent are almost above the valid limit¹⁻³. The contents of this metal can be reduced by treatment of lime, but result is not satisfactory. Thus ion-exchange technique has been proved very useful in this context. The ion exchange resin can be used for metal extraction from ore, analytical reagent, and separation of metal ion and deionization of water⁴⁻¹⁰. Most of commercial ion-exchange resins are sulfonated polystyrene-divinylbenzene copolymer¹¹⁻¹². The use of complex ion-formation in ion-exchange resin has been prepared to solve the problem¹¹⁻¹². The present author¹³ has adopted to prepare and study the new ion-exchange resin. In continuation to this work¹³ the present paper comprises the synthesis of new ion-exchange resin, its ion-exchanging properties and its application for effluents coming out from metal industries. The synthetic route is shown below.

EXPERIMENTAL

Materials

All the chemicals used were of either pure or analytical grade.

Synthesis of polyamines (PA)

The synthesis of polyamine based a 1,4-dichloro methyl benzene and 1,4-benzenediamine was performed by reported method^[14]. The procedure is as follow.

A stoichiometric mixture of 1,4-dichloromethyl benzene, 1,4-benzenediamine and NaHCO₃ in acetone was refluxed for 3 hrs. The resultant polymeric product was washed and air-dried and grind in to fine powder.

Synthesis of PA-triazine resin (PAT resin)

PA (0.1 mole) was transferred in to round bottom flask containing 100 ml THF maintained at 5°C by external cooling and stirred. 7.2 gm (0.1 mole) cyanuric chloride was added to this solution

and pH was brought to 7-8 by adding NaHCO_3 . The whole mass was then stirred for half an hour. The product was filtered and was directly used for further reaction.

Synthesis of PAT-Sulfanilic acid (PATS)

To a mixture of PAT product (0.01 mole) and sulfanilic acid (3.7 g, 0.02 mole) in THF (100 ml), Conc. NaOH was added with maintaining pH 9-10 of the mixture was heated upto 60°C gently for 5 minute and it was stirred at room temperature for 8 hrs. The resulted gel type material was filtered, washed by water and air-dried. It was powdered to 100 mesh size. Yield was 90%. It did not melt up to 300°C and insoluble in water and common organic solvents.

Measurements

The elemental analysis [Table-1] of all PATS sample were estimated by TF-EA-1101 (Italy). The IR spectra were recorded on Nicolet 760 FTIR Spectrophotometer. Sulfanilic acid groups of PATS were determined by known method¹⁵. The batch equilibration method was adopted for the ion-exchanging properties¹⁶⁻¹⁷. The evaluation of the influence of different electrolytes on metal uptake by the polymer, the rate of metal uptake under specified conditions and distribution of various metal ions of different pH values were carried out following the details of the procedures described earlier Table-2 to 4¹⁶⁻¹⁷.

Effluent sample containing heavy metal ions was collected from Jainco electro pleating chemical industry Indore. This sample contained heavy metal ions along with Mg^{+2} , K^+ , Na^+ , NC^- , SO_4^{-2} , F^- paper pulp, clay and turbidity. The characteristics of Jainco electro pleating chemical industry and chemical is reported in table-5.

The procedure adopted to remove heavy metal ions is as follows: 50 ml aliquots of effluents were taken in clean beakers. In each case the pH was adjusted from 6 to 10 with lime 40 mg. triazine derivative of PATS was added and solution was stirred with magnetic stirrer for about 10 minutes.

The solution was transferred to 100 ml measuring cylinder and pH was again checked and allowed to stand for four hours. The whole mass was filtered through whatman filter paper No. 40.

The whole mass was filtered after necessary treatment were used for estimation of metal ions by atomic absorption⁹⁻²⁰. Spectrophotometer model AAS 175. Air acetylene mixture was used as fuel. The results are reported in table-6.

RESULTS AND DISCUSSION

The polymer sample PATS was in form of dark brown powder and insoluble in common organic solvents. It swells up to some extent in conc. NaOH solution. It did not melt up to 300°C . The elemental contents in Table-3 are constituent with the predicted structure. The SO_3H content of PATS are also agreed with the structure. The IR spectrum comprises the bands due to secondly NH (3400 cm^{-1}), methylated group ($2930, 2850, 1430\text{ cm}^{-1}$), s-triazine and aromatic ($3030, 1500, 1600\text{ cm}^{-1}$). The TGA of PATS contains single step degradation. The degradation starts from 280°C , loss rapidly between 300 to 500 and almost lost 85% at 650°C .

Ion-Exchange properties

The examination of data presented in Table-4 reveals that the amount of metal ions taken up by a given amount of the PATS polymer depends upon the nature and concentration of the electrolyte present in the solution. The amounts of Fe^{3+} , Cu^{2+} and UO_2^{2+} ions taken up by the polymer sample increase with the increase in concentration of ions taken up by the polymer sample increase with the increase in concentration of the sulfate ions like chloride, chlorate and nitrate but decrease with the increase in concentration of the sulfate ions. The amounts of the remaining three metal ions Co^{2+} , Mn^{2+} and Zn^{2+} taken by the polymer sample decrease with the increase in concentration of chlorate, chloride, nitrate and sulfate ions.

Rate of metal uptake

The rates of metal absorption by the PATS sample were measured for Fe^{3+} , UO_2^{2+} , Cu^{2+} and Mn^{2+} ions presence of 1 M NaHCO_3 to know the time required to reach the stage of equilibrium. All experiments were carried out at pH 3. The examination of the results presented in Table-5 Shows that UO_2^{2+} and Fe^{3+} ions required slightly more than three hours for the establishment of equilibrium and Cu^{2+} and Mn^{2+} ions required about five hour for the purpose. In the experiments with

Table 1: Analysis of ion exchange resin PATS

Elemental Analysis	C ₃₂ H ₂₆ N ₁₀ O ₄ S ₂ (614)			
	C%	H%	N%	S%
Calculated:	62.54	4.23	22.80	10.42
Found:	62.21	4.10	22.23	10.26
SO ₃ H Groups:	2 Per repeat unit.			
IR features:	3400 (-NH-), 3600-2200 cm ⁻¹ (-OH-) 1604, 1500, 3050 cm ⁻¹ (aromatic), 1520, 1260, 860 (S-triazine). 2930, 2850, 1430 cm ⁻¹ (-CH ₂ -)			

Table 2: Evaluation of the influence of different electrolytes in the uptake of several metal ions; ([Mt (NO₃)₂] = 0.1 mole l⁻¹)^a

Metal ions	pH	[Electrolyte] (mole l ⁻¹)	Adsorption of mmol. .10 ¹ of the metal ion on PATS polymer ^b .			
			NaClO ₄	NaNO ₃	NaCl	Na ₂ SO ₄
Cu ²⁺	5.5	0.01	0.13	0.1	0.16	0.31
		0.05	0.21	0.11	0.17	0.29
		0.1	0.22	0.17	0.18	0.28
		0.5	0.28	0.20	0.21	0.26
		1.0	0.46	0.24	0.27	0.22
Fe ³⁺	2.75	0.01	0.11	0.13	0.01	0.21
		0.05	0.24	0.17	0.03	0.06
		0.1	0.25	0.18	0.07	0.08
		1.0	0.36	0.25	0.25	0.06
UO ₂ ²⁺	4.0	0.01	0.18	0.17	0.16	0.25
		0.05	0.22	0.18	0.18	0.26
		0.1	0.16	0.26	0.21	0.28
		0.5	0.25	0.48	0.24	0.21
Co ²⁺	5.5	1.0	0.56	0.51	0.47	0.19
		0.01	0.18	0.17	0.11	0.08
		0.05	0.18	0.17	0.13	0.09
		0.1	0.08	0.15	0.10	0.06
		0.5	0.04	0.09	0.09	0.05
Mn ²⁺	5.5	1.0	0.03	0.05	0.05	0.02
		0.01	0.17	0.21	0.18	0.14
		0.05	0.15	0.19	0.19	0.11
		0.1	0.11	0.18	0.19	0.04
		0.5	0.10	0.17	0.16	0.02
Zn ²⁺	5.5	1.0	0.07	0.08	0.11	—
		0.01	0.15	0.09	0.12	0.15
		0.05	0.15	0.08	0.12	0.09
		0.1	0.11	0.09	0.07	0.08
		0.5	0.06	0.07	0.02	0.04
		1.0	0.05	0.04	0.01	0.01

a. Volume of electrolyte solution 40 ml, time 24^h, volume of metal ion solution 1 ml, Temp. 25°C.

Wt. of PATS polymer 25 mg.

solution containing UO_2^{2+} and Fe^{3+} ions, more than 70% of equilibrium was established in the first hour. This reveals that the rate of uptake of metal ions follows the order UO_2^{2+} , $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Mn}^{2+}$. The rates of uptake of Zn^{2+} and Co^{2+} ions have been found to be very low at pH 3. Hence the values are not reported.

Distribution ratio of metal ions at different pH values

The results described in Table-6 reveal that the amount of metal ions taken up by the polymer

Table 3: Comparison of the rates of metal (Mt) ion uptake^a

Time (h)	Attainment of equilibrium state ^b			
	Fe^{3+}	UO_2^{2+}	Cu^{2+}	Mn^{2+}
0.5x	66.5	34.8	38.0	19.1
1	75.4	69.3	54.6	46.6
2	91.7	87.8	65.0	62.4
3	94.4	94.2	77.5	76.4
4	97.0	98.9	86.6	84.8
5	-	-	94.4	84.5
6	-	-	95.0	89.4
7	-	-	94.0	94.4

a) $[\text{Mt}(\text{NO}_3)_2] = 0.1 \text{ mole} \cdot \text{l}^{-1}$, volume 1 ml, $[\text{NaNO}_3] = 1 \text{ mol} \cdot \text{l}^{-1}$, volume 40 ml pH = 3, temp 25°C, wt. of PATS polymer 25 mg.

b) Related to the amount of metal ions taken up at the state of equilibrium assumed to be established in 24 h and assumed to be 100%.

Table 4: Distribution ratios, D, of different metal ions as a function of the pH

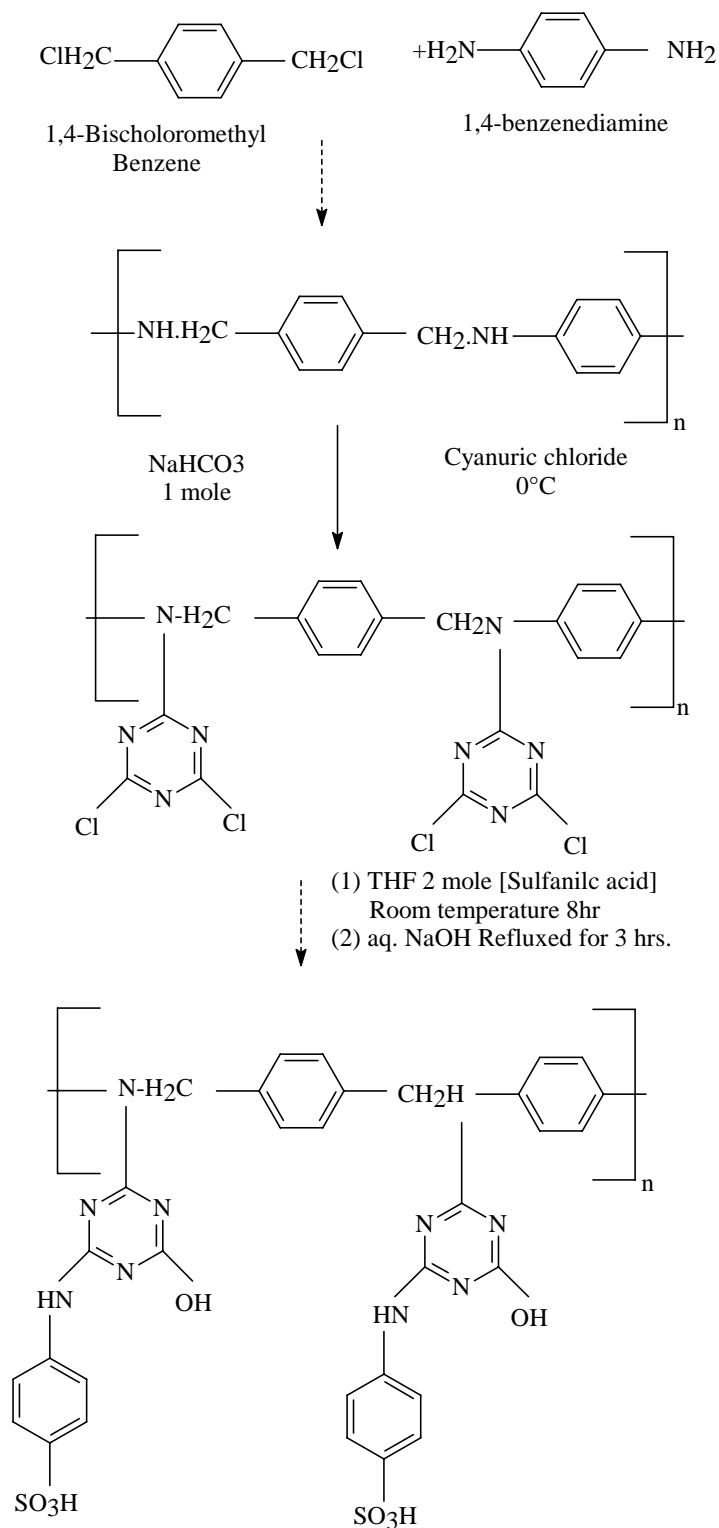
pH	Distribution ration of metal ions					
1.5	-	-	259	-	-	-
1.75	-	128	429	-	-	-
2.0	-	163	516	-	-	-
2.5	-	449	547	-	-	-
3.0	128	946	2798	-	145	-
4.0	246	-	-	5	258	79
5.0	578	-	-	82	336	138
6.0	2809	-	-	341	388	259

sample PATS at equilibrium increases with the increase in pH. The selectivity of the polymer sample UO_2^{2+} and Fe^{3+} ions are higher than that for each of the remaining metal ions. The distribution ratio for Fe^{3+} ions are lower than that for UO_2^{2+} by about 1800 units at pH 3. The lower values of the distribution ratio for Fe^{3+} ions requires its attachment with proper sites on three different polymer chains and that of the UO_2^{2+} ion requires such an attachment with sites on two polymer chains. Among the remaining metal ions, Cu^{2+} has a high value of distribution ratio at pH 6 while the other three metal ions Co^{2+} , Zn^{2+} and Mn^{2+} have a low distribution ratio over a pH range from 4 to 6.

The major part of effluents is generated by mineral and metal processing industries. There is a possibility of recycling of water after suitable treatment. These observations have indicated the necessity to derive more sophisticated method to scavenge the heavy metal ions to a safer limit. The tolerance limit of heavy metals for discharge of effluents into natural stream are different for different metals (e.g. for India Cu-3 ppm, Cd-2.0 ppm, Pb-0.1 ppm Zn-5.0 ppm and Fe-3.0 ppm) the PATS resin reduced the heavy metal ions concentration from effluents to the level much below the discharge limits as shown in table-6. Hence the polymeric reagents can be considered very effective tertiary treatment reagents.

Table 5: Characteristics as effluents contaminated with heavy metal ions obtained from unit of mineral and metal processing industry

Characteristics	Effluents of Jainco Electro Pleating Chemical Industry
Colour	Reddish Brown
pH	5.6
Total hardness	926
Iron	1.13
Copper	0.79
Zinc	6.68
Lead	0.59
Cadmium	0.18
Magnesium	88.20
Calcium	172.1



PATS

Scheme 1

Table 6: Removal of Toxic Metal ion from the Effluents from various Nonferrous Minerals and Processing Industry

Source of effluents	Concentrations of various metal ions (ppm)			
	Metal ions	Untreated effluents	After treatment with lime at 8.0 pH	After treatment with PATS at 8.0 pH
Jainco electro pleating chemical industry	Iron	1.13	Nil	Nil
	Copper	0.79	0.32	Nil
	Zinc	6.68	0.62	0.02
	Lead	0.59	0.12	Nil
	Cadmium	0.18	Nil	Nil
	Magnesium	88.20	88.23	88.23
	Calcium	172.1	172.1	170.0

As shown in table-6 "Mg and Ca: metal ions have not been removed from effluents collected from metallurgical industries when the samples of effluents were treated with resin. Because there was incomplete dissociation of salts of bivalent metals Mg and Ca in these effluents. The absorption of ions also depends upon the degree of cross-linking and nature of functional group in resin.

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